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Effects of microstructure on the hydrogen storage properties of the melt-spun Mg-5Ni-3La (at.%) alloys

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ABSTRACT

Nanocrystalline and amorphous microstructures prepared by rapid solidification (RS) processing are effective in improving the absorption/desorption kinetics of the Mg-based hydrogen storage alloys. In this paper, the as-cast, nanocrystalline and amorphous Mg-5Ni-3La (at.%) alloys were prepared, and effects of microstructure on the hydrogen storage properties of the alloys were studied. The nanocrystalline and amorphous Mg-5Ni-3La (at.%) alloys show better absorption/desorption kinetics than that of the as-cast alloy due to the smaller grain size and more grain boundaries. The values of ΔH (enthalpy) for the Mg-H_2 system of the nanocrystalline and amorphous alloys are -74.0 ± 1.2 kJ mol^{-1} and -66.1 $\pm$ 3.4 kJ mol^{-1}, respectively, which are significantly lower compared to that of the as-cast alloy (-77.7 ± 0.3 kJ mol^{-1}).

1. Introduction

Reversible solid-state hydrogen storage method, including metal hydrides, complex hydrides, MOF etc, is the most promising solution for hydrogen to be used as an energy source [1]. Due to their low cost, great abundance, and high hydrogen storage capacity, Mg-based hydrogen storage alloys have received considerable interest [2–4]. However, sluggish sorption kinetic and high thermodynamic stability of MgH_2 have delayed its commercial applications. Alloying by adding transition metals and rare-earth elements, such as in Mg-Ni [5–7], Mg-RE [8–10], Mg-Ni-RE [11–15] systems, has been used to improve hydrogen storage properties. In addition, methods, for example: ball milling (BM), mechanical alloying (MA) [16–22] and rapid solidification (RS) [23–28], are also effective for altering the hydrogen sorption characteristics of the alloys by obtaining nano-sized grains and even amorphous microstructures. Spassov et al. [23] prepared a series of Mg-Ni-RE alloys (RE = Y, La, Ce) with nanocrystalline and amorphous or partially amorphous microstructures by rapid quenching. The as-quenched $Mg_{75}Ni_{20}Mm_5$ (Mm = Ce, La-rich mischmetal) alloy could absorb 4.0 wt% H_2 in 100 min, which was carried out electrolytically under galvanostatic conditions in 0.5 M KOH at 25 °C and a current density of 10 A/m^2. Lin et al. [29] reported that the hydrogen storage properties of the melt-spun $Mg_3LaNi_{0.1}$ alloy are better than that of the induction-melted $Mg_3LaNi_{0.1}$ alloy. This improvement was attributed to the catalytic role of the in situ formed nanocrystalline Mg_2Ni and LaH_2. Wu et al. [28] have reported that the melt-spun Mg-20Ni-8Mm alloys produced at higher solidification rates contained substantially larger amounts of amorphous phase and fine nano-size particles, which assured an improvement of hydrogen storage properties/performance. Although the beneficial effects of the additions of rare-earth elements are known [23,24,27], an explanation of the hydrogenation behavior of Mg-Ni-Mm alloys containing low amount of Mm and subjected to RS processing is still lacking.

In previous papers by some of the present authors [30,31], hydrogen storage properties of the as-cast Mg-xNi-3La (x = 5, 10, 15, 20 at.%) alloys have been studied. In the present work, combining Mg-5Ni-3La (at.%) alloys obtained using a rapid solidification (RS) process, the effect of microstructure on the hydrogen storage properties of the as-cast, nanocrystalline and amorphous Mg-5Ni-3La (at.%) alloys is studied.

2. Experimental

As-cast Mg-5Ni-3La (at.%) alloy was prepared by induction melting of high-purity magnesium (99.94 wt% purity), nickel (99.96 wt% purity) and lanthanum (99.5 wt% purity) in a vacuum furnace under helium atmosphere. The melt alloys were produced by a single roller melt-spinning technique (copper quenching disc

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with a diameter of 200 mm) in an argon atmosphere of 99.9% purity under a gage pressure of 200 mbar. The velocity of wheel was 11 m/s and 25 m/s, respectively. High-resolution electron microscopy (HREM, JEM-2100F) equipped with an energy-dispersive X-ray spectrometer (EDS) was employed to analyze the nanostructure. The phase structures of the alloys were investigated by X-ray diffraction (XRD, D8 Discover) analysis using Cu Kα ($\lambda_1 = 1.54056$ Å, $\lambda_2 = 1.5444$ Å) radiation. A scanning rate of 0.01°/s was used in the 2θ range from 10° to 90°. The hydrogen storage properties of the Mg-5Ni-3La (at.%) alloys were measured by using an automatically controlled Sieverts-type apparatus (PCT-1SPWIN, Suzuki). The as-cast alloy was crushed and pulverised into powders of −200~+300 mesh in a glove-box filled with purified argon ($H_2O < 0.5$ ppm, $O_2 < 0.5$ ppm) in order to prevent oxidation. While the melt-spun alloys were cut into small pieces, 3–5 mm in length, modified by exposing it to a vapour of concentrated hydrochloric acid during 10–90 s at room temperature. About 0.5 g specimen was used for the characterization of the hydrogen storage properties. After evacuation at 623 K for 1 h, five hydriding/dehydriding cycles at 623 K were performed to make the samples completely activated. Each cycle contained hydrogenation for 1 h under 5 MPa hydrogen pressure and dehydrogenation for 1 h with an initial hydrogen pressure in the channel of 0.2 MPa. There is a vacuum step lasting 0.5 h to ensure that the samples were completely dehydrogenated. The pressure-composition isotherms (PCI) at 548, 573, 598 and 623 K and the hydrogen absorption/desorption kinetics at 623 K with an initial hydrogen pressure in the system of 1.6 MPa H_2, hydriding curves and under the pressure of 0.1 MPa H_2, dehydriding curves were measured.

3. Results and discussion

3.1. Phases and microstructures

In the Mg-5Ni-3La (at.%) system, the alloy contains four phases: Mg, Mg_2Ni, $LaMg_{12}$ and La_2Mg_{17}. As reported in previous publications [30,31], the as-cast Mg-5Ni-3La (at.%) alloy forms an eutectic mixture ($Mg_2Ni + LaMg_x + Mg$) and lamellar microstructures

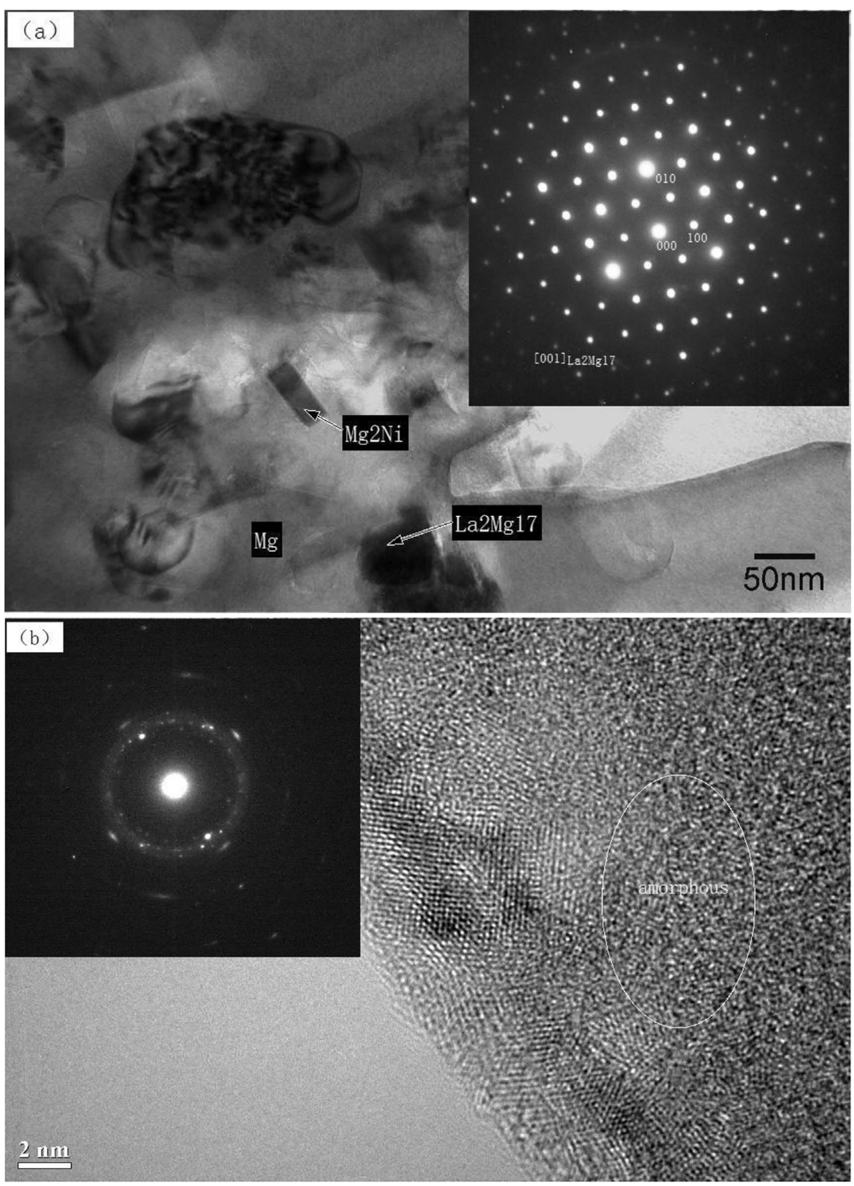

Fig. 1. HRTEM images of the melt-spun Mg-5Ni-3La alloys with a wheel surface velocity of 11 m/s (a) and a wheel surface velocity of 25 m/s (b).